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(54) **Electroluminescent device**

Elektrolumineszente Vorrichtung

Dispositif électroluminescent

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(56) References cited:

**WO-A-95/24056 WO-A-96/08047  
WO-A-96/31909 WO-A-97/32452**

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**EP 0 901 176 B1**

## Description

[0001] This invention relates to electroluminescent devices, especially ones that have a conjugated polymer as a light-emitting layer.

[0002] One type of electroluminescent device is described in PCT/WO90/13148, the contents of which are incorporated herein by reference. The basic structure of this device is a light-emitting polymer film (for instance a film of a poly(p-phenylenevinylene) - "PPV") sandwiched between two electrodes, one of which injects electrons and the other of which injects holes. It is believed that the electrons and holes excite the polymer film, emitting photons. These devices are useful as flat panel displays, in which case one of the electrodes is transparent - for example being made of indium-tin oxide ("ITO").

[0003] One refinement of the device is that to allow the device to display information one of the electrodes can be patterned so that it only injects charge carriers over part of its area. The electrode can be patterned into discrete areas which can be controlled independently and each inject charge carriers into a respective discrete pixel of the polymer film.

[0004] Another refinement is that it has been found that the turn-on voltage, the brightness of the device at low voltage, the efficiency, the lifetime and the stability of the device can sometimes be improved by adding a layer of conductive polymer between the light-emitting film and one of the electrodes. In order to achieve these benefits these conductive polymer layers typically have a sheet resistance less than  $10^6$  Ohms/square the conductivity being controllable by doping of the polymer layer. One example of a suitable conductive polymer is polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDT-PSS") - see EP 0,686,662. For reasons which are discussed in more detail below, it is, however, difficult to produce good devices with an intermediate conductive polymer layer.

[0005] There have been some devices which could be regarded as a hybrid of these refinements. For instance, US 5,399,936 discloses a device in which the patterned electrode is covered by a hole-transporting/injecting organic layer of diphenyl-N-N'-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine ("TPD"). However, the TPD is a small molecule, not a polymer, and it is undoped. WO 96/08047 discloses a device in which a conductive polymer layer is patterned to provide insulative regions and conductive regions to pixellate the display.

[0006] According to the present invention there is provided an electroluminescent device comprising: a first charge-carrier injecting layer for injecting positive charge carriers and a second charge-carrier injecting layer for injecting negative charge carriers, at least one of the charge-carrier injecting layers being patterned so as to comprise spaced-apart charge-injecting regions; an organic light-emitting layer located between the first and second charge-carrier injecting layers; and an un-

patterned conductive polymer layer located between the organic light-emitting layer and the patterned charge-carrier injecting layer, the resistivity of the conductive polymer layer being sufficiently low to allow charge carriers to flow through it from the charge-injecting regions to generate light in the organic light-emitting layer but sufficiently high to resist lateral spreading of charge carriers beyond the charge-injecting regions.

[0007] The patterned charge injecting layer could be an anode or a cathode. The other charge injecting layer (of opposite polarity) may be patterned or unpatterned. The width of the charge injecting regions is suitably less than 1mm, 300µm or 100µm, preferably less than 50µm and most preferably less than or around 20µm. The spacing between the charge injecting regions is suitably less than 1mm, 300µm or 100µm, preferably less than 50µm and most preferably less than or around 20µm.

[0008] The cathode is preferably a sputtered cathode. The cathode is preferably a low work function cathode. The cathode may be patterned by dry etching.

[0009] The light-emitting layer preferably is or comprises a semiconductive conjugated polymer such as PPV. The light-emitting layer suitably is or comprises PPV, poly(2-methoxy-5(2'-ethyl)hexyloxyphenylene-vinylene) ("MEH-PPV"), a PPV-derivative (e.g. a di-alkoxy derivative), a polyfluorene and/or a co-polymer incorporating polyfluorene segments, PPVs and/or related copolymers. It could be deposited by spin-coating, dip-coating, blade-coating, meniscus-coating, self-assembly etc. The constituent of the light-emitting layer and/or its precursor is suitably water-based: examples are precursor-based PPVs. The thickness of the light-emitting layer is preferably in the range from 20 to 200nm and most preferably around 100nm.

[0010] The term "conjugated" indicates a polymer for which the main chain is either fully conjugated, possessing extended pi molecular orbitals along the length of the chain, or is substantially conjugated, but with interruptions to conjugation at various positions, either random or regular, along the main chain. It includes within its scope homopolymers and copolymers.

[0011] The conductive polymer layer preferably is or comprises polyethylene dioxythiophene ("PEDT"), polystyrene sulphonic acid doped polyethylene dioxythiophene ("PEDT-PSS"), doped polyaniline, a doped alkylthiophene and/or a doped polypyrrole. The thickness of the layer is suitably less than 200nm, preferably less than 100nm and most preferably less than or around 50nm. The sheet resistance of the layer is suitably greater than  $10^6$  or  $10^7$  Ohms/square, preferably greater than  $10^8$  Ohms/square and most preferably greater than or around  $10^{10}$  Ohms/square.

[0012] The conductivity of the conductive polymer layer is preferably adjustable (e.g. by means of additive components) over a relatively wide range. The conductive polymer is preferably doped with one or more components that influences its conductivity (e.g. polystyrene sulphonic acid ("PSS") or epoxy-silane). The conductive

polymer is suitable polyaniline, polypyrrole or a poly-thiophene.

[0013] The conductive polymer is preferably adapted to reduce its solubility and/or its interaction with an adjacent layer, especially a polymer layer. This layer is preferably the subsequent layer and most preferably the light emitting layer. To achieve this the conductive polymer preferably contains an additional component. This component is suitably a cross-linking agent (e.g. epoxy-silane). This component preferably does not significantly impair the performance of the device, especially by increasing the drive voltage significantly, reducing the emission uniformity significantly or reducing the efficiency significantly. This component is especially advantageous in a device in which the conductive polymer and the light-emitting layer have the same or similar solvents. The amount of this component in the conductive polymer layer is suitably greater than 50wt%, preferably between 50wt% and 200wt% and most preferably around 100wt%.

[0014] Where the conductive polymer is PEDT-PSS the dilution of the PEDT-PSS with the PSS is preferably greater than 20% and most preferably greater than 50%. Any of these proportions may be used together with any of the proportions of epoxy-silane disclosed above.

[0015] The resistance of the conductive polymer layer is suitably such as to require an increase in the drive voltage of the device (compared to when the layer is absent) of 0.5V or less (preferably 0.2V or less) for equivalent device performance.

[0016] The present invention will now be described by way of example with reference to the accompanying drawings, in which:

figure 1 shows a cross-section of an electroluminescent device; and

figure 2 shows the chemical formula of PEDT-PSS.

[0017] Figure 1 shows an electroluminescent device having an anode layer 1 for injecting positive charge carriers, a conductive polymer layer 2, an organic light-emitting layer 3 and a cathode layer 4 for injecting negative charge carriers. The anode is patterned so as to comprise charge-injecting regions 5 (defining pixels) which are spaced from each other by gaps 6. The conductivity of the conductive polymer layer is selected so as to be low enough to allow for normal operation of the device (for instance, not so high that the drive voltage is increased significantly or that the efficiency or uniformity drops significantly) but high enough to resist cross-talk and lateral current-spreading between the charge-injecting regions and to resist off-pixel emission (so that the pixel edges are sharp and well-defined and there is no fuzzy emission edge to the pixels).

[0018] In more detail, the anode 1 is a layer of indium-tin oxide ("ITO") having a thickness of approximately 150nm. The widths of the pixel regions 5 and the gaps 6 are around 50µm.

[0019] The conductive polymer layer is a layer of PEDT-PSS with a thickness of around 50nm and a conductivity of around  $10^8$  Ohms/square. The layer also contains around 100wt% epoxy-silane to produce cross-linking.

[0020] The light-emitting layer 3 is a layer of PPV having a thickness of 100nm.

[0021] The cathode 4 is a layer of aluminium, having a thickness of 150nm.

[0022] The relatively high resistance of the conductive polymer layer resists cross-talk between the charge-injecting regions 5, with lateral off-pixel emission being restricted to within 10 or 5% of the pixel dimension and/or leakage of current outside the pixel boundary being restricted to 5 or 10% of the total current through the addressed pixel. And surprisingly, it has been found that even at conductivities of the conductive polymer layer as low as  $10^{10}$  Ohms/square the performance of the device is not necessarily impaired, the increase in drive voltage required being minimal.

[0023] A rough guide to the conductivity of the polymer layer that is required can be estimated with the aid of the following relationships:

for isotropic homogeneous conductivity media, the voltage drop across a device is given by:

$$V_d = j_{\perp} R_{\square} t^2$$

$j$  = current / area

$t$  = thickness in units of  $\text{area}^{-1}$

$R_{\square}$  = sheet resistivity in  $\Omega/\square$

whereas the current between the ITO lines is:

$$j_{\parallel} = (V/A) / R_{\square}$$

$A$  = aspect ratio of space between ITO lines

[0024] Clearly, the minimum advisable thickness of the polymer layer is dependant on the reliability of the process used to deposit the layer - if the layer is uneven and too thin in places then the anode and the light-emitting layer could make contact.

[0025] To produce the device, first the anode is deposited (on a glass substrate 7 for example) and patterned, e.g. by laser scribing, to define the charge-injecting and non-charge injecting regions. The charge-injecting regions are connected individually to a control circuit so that they can be controlled independently and can thereby define pixel regions of the display, with each pixel region forming a column extending up from the corresponding charge injecting region.

[0026] A PEDT-PSS solution having a ratio of PEDT to PSS of 1:1.6 and a solid content of 1.2 to 1.3% is diluted further with extra PSS to achieve a PEDT to PSS ratio of 1:55 and a solid content of about 1%. Around

100wt% epoxy-silane (specifically 3-glycidy oxypropyltrimethoxysilane) is then added to the solution and the mixture is deposited on to the anode by spin coating. It is believed that both the PSS and the epoxy-silane act to reduce the conductivity of the resulting layer. The combination of PSS and epoxy-silane also helps to avoid problems with leakage currents in the pixels which have been experienced when epoxy-silane is used with lower concentrations of PSS. (Further information on this polymer system, which is available from Bayer AG, is given in Bayer's Provisional Product Information Sheet for Trial Product AI 4071).

[0027] After the PEDT-PSS layer has dried the layer of PPV is deposited on to the layer of PEDT-PSS by spin-coating from an aqueous solvent. This process is of itself well-known. It has been experienced that depositing a PPV precursor in this way on top of a layer of PEDT-PSS can dissolve the underlying PEDT-PSS layer, causing non-uniformities in, for instance, the thickness of the layer structure. This can result in non-uniform emission. It has been found that this problem is increased for higher concentrations of PSS in the PEDT-PSS layer, although higher concentrations of PSS can provide advantages in the device's current-voltage characteristics (e.g. less current leakage below the turn-on voltage and in reverse bias) and lifetime. Depositing PPV over a PEDT-PSS layer has also been found to reduce the resistance of the PEDT-PSS layer. However, with epoxy-silane added to the PEDT-PSS layer the layer has been found to be structurally more stable, even at relatively high concentrations of PSS, avoiding the problems of intermixing with a PPV precursor and reduced resistance.

[0028] The cathode is then deposited by sputtering over the PPV layer, for instance by DC magnetron sputtering according to the following procedure. A target of Al95%/Li2.5%/Cu1.5%/Mg1% is used with sputtering in constant power mode at around  $3.2\text{Wcm}^{-2}$  (100mm diameter target and 250W), pressure around  $5 \times 10^{-3}$  mbar at 25sccm argon flow (base pressure around  $1 \times 10^{-6}$  mbar), target voltage 400-410V, target-substrate distance 75mm and a deposition rate of around 1nm/s. This tends to produce a metallic cathode of compact morphology with low average grain size and good adhesion to the adjacent organic layer.

[0029] When the device is in operation a voltage is applied across the electrodes and electrons and holes combine in the light emitting region to generate (via, it is believed, excitons) photons which are emitted through the ITO electrode and the glass layer. The recombination process is independent of the physical layering of the device.

[0030] Some alternative embodiments will now be described.

[0031] The light-emitting layer could be PPV (yellow/green) via the precursor route - as described above - or MEH-PPV (orange/red) which could be deposited from an organic solvent.

[0032] Other suitable polymers for the conductive polymer layer include polyaniline, polypyrrole and other polythiophenes than PEDT-PSS. In each case, suitable dopants and/or cross linking agents could be added to influence the polymer's properties.

[0033] The layer of conductive polymer could be deposited by a number of methods, including dip-coating, meniscus-coating, self-assembly or doctor-blade-coating.

[0034] Instead of the entire conductive polymer region being unpatterned, some parts of it could be unpatterned and some patterned.

[0035] The cathode could be a calcium cathode, deposited for instance by evaporation.

[0036] Some potential applications for the device are dot-matrix displays including passive matrix displays and active matrix addressed displays. In these devices, each charge-injecting region of the anode typically can selectively provide charge carriers to more than one pixel.

[0037] In view of the foregoing description it will be evident to a person skilled in the art that various modifications may be made within the scope of the invention.

## Claims

1. An electroluminescent device comprising:

a first charge-carrier injecting layer for injecting positive charge carriers and a second charge-carrier injecting layer for injecting negative charge carriers, at least one of the charge-carrier injecting layers being patterned so as to comprise spaced-apart charge-injecting regions;  
an organic light-emitting layer located between the first and second charge-carrier injection layers; and  
an unpatterned conductive polymer layer comprising polypyrrole or a polythiophene located between the organic light-emitting layer and the patterned charge-carrier injecting layer, the resistivity of the conductive polymer layer being sufficiently low to allow charge carriers to flow through it from the charge-injecting regions to generate light in the organic light-emitting layer but sufficiently high to resist lateral spreading of charge carriers beyond the charge-injecting regions.

2. An electroluminescent device as claimed in claim 1, wherein the light-emitting layer comprises a light-emitting conductive polymer.

3. An electroluminescent device as claimed in claim 1, wherein the light-emitting layer comprises a semiconductive conjugated polymer.

4. An electroluminescent device as claimed in any preceding claim, wherein the conductive polymer layer comprises polyethylene dioxythiophene.
5. An electroluminescent device as claimed in any preceding claim, wherein the conductive polymer layer comprises an additive component, the presence of which affects the resistivity of the conductive polymer layer.
6. An electroluminescent device as claimed in claim 5, wherein the additive component is polystyrene sulphonic acid.
7. An electroluminescent device as claimed in claim 5 or 6, wherein the conductive polymer layer contains greater than 50% of the additive component.
8. An electroluminescent device as claimed in any preceding claim, wherein the conductive polymer layer comprises a component which reduces the solubility of the layer.
9. An electroluminescent device as claimed in claim 8, wherein the component is epoxy-silane.
10. An electroluminescent device as claimed in claim 8 or 9, wherein the conductive polymer layer contains great than 50wt% of the component.
11. An electroluminescent device as claimed in any preceding claim, wherein the sheet resistance of the conductive polymer layer is greater than  $10^6$  Ohms/square.
12. An electroluminescent device as claimed in any preceding claim, wherein the regions of the light emitting layer capable of emitting light in use do not extend laterally beyond the charge injecting regions by more than 10% of the width of the charge injecting regions.
13. An electroluminescent device as claimed in any preceding claim, wherein each charge-injecting region defines one or more pixel regions of the device.
14. An electroluminescent device as claimed in any preceding claim, wherein each charge-injecting region is independent of the or each other charge-injecting region.
15. An electroluminescent device as claimed in any preceding claim, wherein the first charge-carrier injecting layer is the patterned charge-carrier injecting layer.

## Patentansprüche

1. Elektrolumineszierende Anordnung, welche aufweist:  
 eine erste Ladungsträger-Injektionsschicht zum Injizieren positiver Ladungsträger und eine zweite Ladungsträger-Injektionsschicht zum Injizieren negativer Ladungsträger, wobei wenigstens eine der Ladungsträger-Injektionsschichten derart mit einem Verteilungsmuster versehen ist, das die Ladungs-Injektionsbereiche enthält, die in gegenseitigem Abstand angeordnet sind;  
 eine organische lichtemittierende Schicht, die zwischen den ersten und zweiten Ladungsträger-Injektionsschichten angeordnet ist; und  
 eine nicht mit einem Verteilungsmuster versehene leitende Polymerschicht, die Polypyrrol oder ein Polythiophen enthält und zwischen der organischen lichtemittierenden Schicht und der mit einem Verteilungsmuster versehenen Ladungsträger-Injektionsschicht angeordnet ist, wobei der spezifische Widerstand der leitenden Polymerschicht ausreichend niedrig ist, um ein Fließen der Ladungsträger durch dieselbe von den Ladungs-Injektionsbereichen zu ermöglichen, so dass Licht in der organischen lichtemittierenden Schicht erzeugt wird, jedoch ausreichend hoch ist, um einer seitlichen Ausbreitung von Ladungsträgern über die Ladungs-Injektionsbereiche hinaus zu widerstehen.
2. Elektrolumineszierende Anordnung nach Anspruch 1, bei welcher die lichtemittierende Schicht ein lichtemittierendes leitendes Polymer enthält.
3. Elektrolumineszierende Anordnung nach Anspruch 1, bei welcher die lichtemittierende Schicht ein halbleitendes konjugiertes Polymer enthält.
4. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher die leitende Polymerschicht Polyethylen-Dioxythiophen enthält.
5. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher die leitende Polymerschicht eine additive Komponente enthält, deren Anwesenheit den spezifischen Widerstand der leitenden Polymerschicht beeinflusst.
6. Elektrolumineszierende Anordnung nach Anspruch 5, bei welcher die additive Komponente Polystyrol-Sulfonsäure ist.
7. Elektrolumineszierende Anordnung nach Anspruch 5 oder 6, bei welcher die leitende Polymerschicht

mehr als 50% der additiven Komponente enthält.

8. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher die leitende Polymerschicht eine Komponente enthält, welche die Löslichkeit der Schicht verringert. 5
9. Elektrolumineszierende Anordnung nach Anspruch 8, bei welcher die Komponente Epoxy-Silan ist. 10
10. Elektrolumineszierende Anordnung nach Anspruch 8 oder 9, bei welcher die leitende Polymerschicht mehr als 50 Gew.-% der Komponente enthält.
11. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher der Schichtwiderstand der leitenden Polymerschicht mehr als  $10^6$  Ohm/Square beträgt. 15
12. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher die zum Emittieren von Licht fähigen Bereiche der lichtemittierenden Schicht bei Gebrauch sich nicht seitlich über die Ladungs-Injektionsbereiche um mehr als 10% der Breite der Ladungs-Injektionsbereiche hinaus erstrecken. 20 25
13. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher jeder Ladungs-Injektionsbereich einen oder mehrere Pixel-Bereiche der Anordnung definiert. 30
14. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher jeder Ladungs-Injektionsbereich von dem oder jedem anderen Ladungs-Injektionsbereich unabhängig ist. 35
15. Elektrolumineszierende Anordnung nach einem der vorangehenden Ansprüche, bei welcher die erste Ladungsträger-Injektionsschicht die mit einem Verteilungsmuster versehene Ladungsträger-Injektionsschicht ist. 40

#### Revendications 45

1. Dispositif électroluminescent, comprenant:

une première couche d'injection de porteurs de charge pour injecter des porteurs de charge positive, et une deuxième couche d'injection de porteurs de charge pour injecter des porteurs de charge négative, au moins une des couches d'injection de porteurs de charge étant configurée de manière à comprendre des régions d'injection de charge espacées; 50  
une couche d'émission de lumière organique située entre les première et deuxième couches 55

d'injection de porteurs de charge; et une couche de polymère conducteur non configurée comprenant du polypyrrole ou un polythiophène, située entre la couche d'émission de lumière organique et la couche d'injection de porteurs de charge configurée, la résistivité de la couche de polymère conducteur étant suffisamment basse pour permettre aux porteurs de charge de s'écouler librement à travers elle à partir des régions d'injection de charge afin de générer de la lumière dans la couche d'émission de lumière organique, mais suffisamment élevée pour résister à la dispersion latérale des porteurs de charge au-delà des régions d'injection de charge.

2. Dispositif électroluminescent selon la revendication 1, dans lequel la couche d'émission de lumière comprend un polymère conducteur émettant de la lumière.
3. Dispositif électroluminescent selon la revendication 1, dans lequel la couche d'émission de lumière comprend un polymère conjugué semi-conducteur.
4. Dispositif électroluminescent selon la revendication 1, dans lequel la couche de polymère conducteur comprend du dioxythiophène de polyéthylène.
5. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel la couche de polymère conducteur comprend un composant d'additif dont la présence affecte la résistivité de la couche de polymère conducteur.
6. Dispositif électroluminescent selon la revendication 5, dans lequel le composant d'additif est l'acide sulfonique de polystyrène.
7. Dispositif électroluminescent selon la revendication 5 ou 6, dans lequel la couche de polymère conducteur contient plus de 50 % du composant d'additif.
8. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel la couche de polymère conducteur comprend un composant qui réduit la solubilité de la couche.
9. Dispositif électroluminescent selon la revendication 8, dans lequel le composant est l'époxy-silane.
10. Dispositif électroluminescent selon la revendication 8 ou 9, dans lequel la couche de polymère conducteur contient plus de 50 % en poids du composant.
11. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel la résistance de feuille de la couche de polymère con-

ducteur est plus élevée que  $10^6$  Ohms/carré.

12. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel les régions de la couche d'émission de lumière capables d'émettre de la lumière lors de l'utilisation ne s'étendent pas latéralement au-delà des régions d'injection de charge de plus de 10 % de la largeur des régions d'injection de charge. 5
- 10
13. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel chaque région d'injection de charge définit une ou plusieurs régions de pixels du dispositif. 15
14. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel chaque région d'injection de charge est indépendante de la ou de chaque autre région d'injection de charge. 20
- 25
15. Dispositif électroluminescent selon l'une quelconque des revendications précédentes, dans lequel la première couche d'injection de porteurs de charge est la couche d'injection de porteurs de charge configurée. 25

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FIG. 1

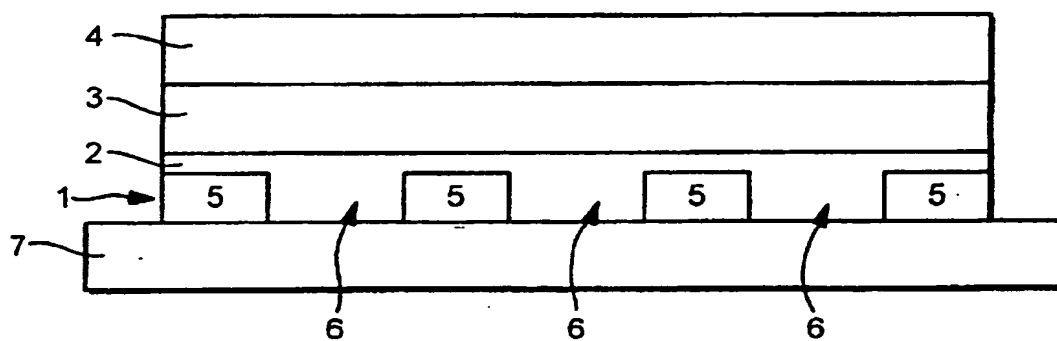


FIG. 2

